A simulation model for fate and transport of methyl bromide during fumigation in plastic-mulched vegetable soil beds[†]

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Abstract: A coupled water-heat and chemical transport model was used to describe the fate and transport of methyl bromide fumigant in low-density polyethylene plastic-mulched soil beds used for vegetable production. Methyl bromide transport was described by convective-dispersive processes including transformations through hydrolysis. Effects of non-isothermal conditions on chemical transport were considered through inclusion of temperature effects on transport parameters. An energy-balance approach was used to describe the plastic-mulched boundary condition that controls the thermal regime within the soil bed. Simulations were made for variable water-saturation regimes within the bed and for different depths of fumigant injection. Simulations for various scenarios revealed that large amounts (20–44% over a 7-day period) of applied methyl bromide are lost from the un-mulched furrows between the beds. Plastic mulching of the bed was found to be only partially effective (11–29% emission losses over a 7-day period) in reducing atmospheric emissions. Deep injection of fumigant and saturating the soil with water both led to increased retention of methyl bromide within the soil and less emission to the atmosphere. However, deep injection was unfavorable for effective sterilization of the crop root zone.

Keywords: methyl bromide; plastic mulch; fumigation; volatilization; hydrolysis; multiphase transport; numerical model

1 INTRODUCTION

Methyl bromide (MeBr) is used in the USA on more than 100 crops as a soil fumigant, a post-harvest treatment or as a plant quarantine treatment to control a variety of pests. MeBr is utilized heavily as an effective agricultural fumigant during vegetable and fruit production in Florida, California and Hawaii. In the USA, strawberries (16% of the US total production) and tomatoes (24% of the US total production) are the crops which use the most MeBr, consuming ≈6500 tons annually. Other crops for which this pesticide is used as a soil fumigant include tobacco, peppers, grapes and nut crops.[1] Selected chemical and physical properties of MeBr are shown in Table 1.[2] MeBr, a broad-spectrum pesticide, is highly effective for eradicating a variety of pests. Although MeBr is a significant stratospheric ozone-depleting substance, recent investigations imply that it should not accumulate in the atmosphere.[1,3,4] Thus, the economic value and efficacy of MeBr fumigation to control pests in agricultural soils warrant renewed research efforts. Modeling MeBr fate and transport during agricultural use (soil fumigation) is particularly needed to provide improved insight into system dynamics with regard to atmospheric emissions resulting from MeBr fumigation, and to provide guidelines for future research needs.

Table 1. Selected chemical and physical properties of methyl bromide (CH_3Br, bromomethane) (Adapted from Reference 2)

Selected property	*Magnitude*
Relative molecular mass	94.94
Boiling point (°C)	4.6
Solubility in water at 20 °C (g kg^{-1})	13.4
Gas density at 20 °C (g litre^{-1})	3.974
Diffusion coefficient in free air at 20 °C (cm h^{-1})	325.08
Henry's Law constant at 20 °C	0.251
Vapor pressure at 20 °C (mm Hg)	1420
Hydrolysis rate in soil (h^{-1})[a]	0.014
Octanol–water partition coefficient (K_{oc}; cm^{-3} g^{-1})[b]	22

[a] From Reference 8.
[b] From Reference 31.

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MeBr losses to the atmosphere during soil fumigation are recognized, and attempts have been made to quantify them through field experiments. Under conventional fumigation practices of covering the field with polyethylene plastic film (also referred as tarp) after MeBr injection, 30–60% of the applied MeBr has been estimated to escape to the atmosphere.[5–7] In California, initial emission fluxes through polyethylene plastic films covering the entire fumigated soil area have been reported to be as high as $\sim 10.0\,\mathrm{g\,m^{-2}\,day^{-1}}$[8] and $\sim 16.5\,\mathrm{g\,m^{-2}\,day^{-1}}$,[9] and predicted overall emission was 53% during the first 5 days after fumigation.[9] For MeBr fumigation under plastic-mulched beds with uncovered furrows between the beds in Florida, the emission fluxes from mulched beds following fumigation were reported as high as $\sim 5.0\,\mathrm{g\,m^{-2}\,day^{-1}}$ (February, 1996) and $\sim 50.0\,\mathrm{g\,m^{-2}\,day^{-1}}$ (June, 1995).[10]

Only a few prior modeling efforts have attempted to describe MeBr transport in soil during fumigation. Hemwall[11,12] described a two-dimensional (2-D) model for gaseous diffusion of MeBr in soil with a low water content. The model assumed uniform soil water content and isothermal soil conditions. Siebering and Leistra[13] presented a one-dimensional (1-D) model for gaseous diffusion of MeBr under isothermal conditions. Water content was held constant and small, such that water flow could be ignored. Model simulations for a greenhouse experiment matched experimental results only in the upper part of the soil profile (to 40 cm) and deviated substantially elsewhere.

Rolston and Glauz[14] proposed a model describing radial diffusive transport of gaseous MeBr away from injection chisels during fumigation of a field profile. Although the model was based on similar work done by Hemwall[11,12] and Siebering and Leistra,[13] the dissolution-distillation of MeBr gas on soil solids and in soil water was included, using both kinetic and equilibrium relationships and hydrolysis to yield Br^- ions according to first-order kinetics. The model considered the case in which the soil surface was fully covered with a barrier totally impermeable to the diffusion of gas, as well as the case of a bare soil surface. Reported simulation results were compared with the experimental data of Abdalla *et al*,[15] which involved a mulch barrier. The model simulations could match the experimental data only when no barrier was considered as an upper boundary condition, contrary to experimental conditions. Sensitivity analysis of input parameters showed reaction kinetics to be unimportant, so they could safely be ignored. Water flow and non-isothermal temperature effects were ignored in all simulations. Also, the boundary conditions at the soil surface were unrealistically handled by making the plastic mulch impermeable and applying a zero-concentration fixed boundary condition at the soil surface.

Recently Wang *et al*[9] adopted a 2-D finite-element model, CHAIN_2D[16] to simulate the fate and transport of MeBr fumigant in soil. CHAIN_2D numerically solves the partial differential equations for 2-D, uncoupled water and heat flows and solute transport in variably saturated porous medium. Various temperature-dependent coefficients (such as diffusion, Henry's Law constant, etc) were included. However, the model lacked a realistic description of the soil-surface boundary by ignoring the effects of plastic mulch on the thermal regime of the underlying soil. Placement of plastic mulch significantly changes the energy balance at the soil/atmospheric interface[17] and requires proper definition of the energy exchange and balance at the interface to simulate non-isothermal soil conditions. Although a cyclic nature of emission flux in accordance with non-isothermal conditions was demonstrated, model simulations failed to accurately describe the cyclic field-measured emission flux reported by Yates *et al.*[18]

It is thus evident that, in modeling MeBr fate and transport, various investigators have made simplifying assumptions (such as small and constant soil water content and isothermal conditions) that do not reflect realistic field conditions. Moreover, boundary conditions at the soil surface, which should be more realistically described by a Neumann-type in the case of MeBr fumigation, have been improperly designated (such as a zero-concentration fixed boundary condition at nodes exposed to the atmosphere for uncovered soil). The temperature-dependent dissolution (Henry's Law constant) and diffusion (both in air and water) of MeBr, and variably saturated soil-water flow are common occurrences under field conditions that cannot be ignored. This is particularly true for humid climates.

Plastic mulching of soil so strongly affects the soil thermal regime that it has been used to exterminate soil-borne pathogens by heating the soil to an excessively high temperature through a process called soil solarization. Ham *et al*[17] measured soil temperature at 10-cm depths beneath five different plastic mulches. The highest temperatures were observed beneath a black plastic mulch, which strongly absorbed shortwave radiation, and cooler temperatures beneath 'aluminium-paint-on-black' plastic-mulch and 'white paint-on-black' plastic mulches. The aluminium-painted and white-painted plastic mulches had high shortwave reflectance. Ham and Kluitenberg[19] developed a mechanistic model for simulating the energy and temperature regimes of a field surface covered by plastic mulch including the optical properties of plastic mulches. The application of their model to the field data of Ham *et al*[17] was shown to predict the observed thermal regime with reasonable accuracy.

The model used in the present investigation represents improvements over earlier efforts.[11,13,14] Coupled transient flows of both heat and water based upon Philip–deVries theory is included.[20] Plastic-mulch boundary conditions are realistically described, adapting the mechanistic model of Ham and Kluitenberg,[19] by inclusion of optical properties of the plastic mulch in the energy balance at the soil/atmospheric interface. This model provides an opportunity to consider the effects of improved temperature and water content estimates upon estimates of chemical transport (both in the liquid and gaseous phases). The objectives of this study were to:

1 investigate important processes influencing MeBr fate and transport, including volatilization and degradation in fumigated soil beds used for vegetable and fruit production in Florida,
2 investigate the effects of non-isothermal and variably saturated soil conditions on material balance of MeBr during simulated fumigations, and
3 evaluate effectiveness of the current management technique-, ie plastic mulching of soil beds to minimize MeBr emissions from fumigated soil beds to the atmosphere.

2 MODEL DESCRIPTION

A finite-element numerical model developed by Shinde *et al*[21] was modified in order to simulate 2-D coupled water-heat flows and chemical transport in a variably saturated heterogenous soil.[22] The chemical of interest was assumed to exist in three environmental phases; ie the solid, liquid and gaseous phases of the soil. The model includes a detailed thermal surface boundary condition for plastic-mulched soil surfaces in parallel soil-bed systems used for vegetable/fruit production. An energy balance model that incorporates optical properties of the plastic material determines the diurnal atmospheric exchange of energy and its effect on soil temperature.[19]

The original water content-based formulation of Philips–deVries theory[20] was modified by Milly and Eagleson[23] to provide

$$\left[\left(1-\frac{\rho_v}{\rho_L}\right)\frac{\partial\theta_L}{\partial h}+\frac{\theta_a}{\rho_L}\frac{\partial\rho_v}{\partial h}\right]\frac{\partial h}{\partial t} = \nabla[(K+D_{hv})\nabla h+D_{Tv}\nabla T+Kk] - \left[\left(1-\frac{\rho_v}{\rho_L}\right)\frac{\partial\theta_L}{\partial T}+\frac{\theta_a}{\rho_L}\frac{\partial\rho_v}{\partial T}\right]\frac{\partial T}{\partial t} \qquad (1)$$

where ρ_v ($\mathrm{g\,cm^{-3}}$) is water vapor density, ρ_L ($\mathrm{g\,cm^{-3}}$) is soil water density, θ_L ($\mathrm{cm^3\,cm^{-3}}$) is soil volumetric water content, θ_a ($\mathrm{cm^3\,cm^{-3}}$) is the soil volumetric air content, h (cm) is matric potential, T (K) is temperature, t (h) is time, K ($\mathrm{cm\ h^{-1}}$) is hydraulic conductivity, k ($\mathrm{cm\,h^{-1}}$) is the vertical unit vector, D_{hv} ($\mathrm{cm\ h^{-1}}$) is the isothermal vapor diffusivity, and D_{Tv} ($\mathrm{cm\ h^{-1}\ K^{-1}}$) is the thermal vapor diffusivity. Equation (1) describes both liquid water and vapor water flow in response to gradients of matric potential and thermal energy.

Coupled heat flow in the soil in response to gradients of temperature and pressure-head has been described by[23,24]

$$\left(C+H_1\frac{\partial\rho_v}{\partial T}+H_2\frac{\partial\theta_L}{\partial T}\right)\frac{\partial T}{\partial t} = \nabla[\lambda\nabla T+\rho_L L D_{hv}\nabla h - C_L(T-T_o)q_w] - \left(H_1\frac{\partial\rho_v}{\partial h}+H_2\frac{\partial\theta_L}{\partial h}\right)\frac{\partial h}{\partial t} \qquad (2)$$

and

$$C = C_d + C_L\rho_L\theta_L + C_v\rho_v\theta_a \qquad (3a)$$

$$H_1 = [L_o + C_v(T-T_o)]\theta_a \qquad (3b)$$

$$H_2 = (C_L\rho_L - C_v\rho_v)(T-T_o) - \rho_v L_v \qquad (3c)$$

where λ ($\mathrm{J\,cm^{-1}\,h^{-1}\ K^{-1}}$) is thermal conductivity, L ($\mathrm{J\,g^{-1}}$) is latent heat of vaporization, q_w ($\mathrm{cm\ h^{-1}}$) is total water flux (liquid + vapor), C_d ($\mathrm{J\,cm^{-3}\ K^{-1}}$) is volumetric dry heat capacity of the soil; C_L ($\mathrm{J\,g^{-1}\ K^{-1}}$) and C_v ($\mathrm{J\,g^{-1}\ K^{-1}}$) are specific heat of liquid water and vapor water, respectively; and the subscript $_o$ implies the magnitude at a designated reference level.

Dispersive transport and hydrolysis of MeBr in the model were described mathematically as

$$\frac{\partial q_L c_{MBr}}{\partial t}+\frac{\partial\rho s_{MBr}}{\partial t}+\frac{\partial q_a g_{MBr}}{\partial t} = \nabla(q_L D^L_{MBr}\nabla c_{MBr}) + \nabla(q_a D^g_{MBr}\nabla g_{MBr}) - \nabla(q_L c_{MBr}) - \mu_{L,MBr}q_L c_{MBr} \qquad (4)$$

$$\frac{\partial q_L c_{Br}}{\partial t} = \nabla(q_L D^L_{Br}\nabla c_{Br}) - \nabla(q_L c_{Br}) + \mu_{L,MBr}q_L c_{MBr} \qquad (5)$$

where ρ ($\mathrm{g\,cm^{-3}}$) is soil bulk density; s ($\mathrm{g\,g^{-1}}$) represents adsorbed concentrations; c ($\mathrm{g\,cm^{-3}}$) is concentration in water; g ($\mathrm{g\,cm^{-3}}$) is concentration in the soil gaseous phase; q_L ($\mathrm{cm\ h^{-1}}$) is liquid water flux; $\mu_{L,\ MBr}$ ($\mathrm{h^{-1}}$) is the first-order (hydrolysis) rate constant for MeBr in the liquid phase; D^L ($\mathrm{cm^2\,h^{-1}}$) is the dispersion coefficient for the liquid phase; and D^g ($\mathrm{cm^2\,h^{-1}}$) is the diffusion coefficient for the gas phase.

Partitioning of MeBr molecules between liquid-solid and liquid-gaseous phases was considered through linear relationships defining the sorption coefficient ($k_{d,\ MBr}$; $\mathrm{ml\,g^{-1}}$) and Henry's Law constant ($k_{g,\ MBr}$; dimensionless), respectively, as

$$g_{MBr} = k_{g,MBr}c_{MBr} \qquad (6)$$

$$S_{MBr} = k_{d,MBr}c_{MBr} \qquad (7)$$

The temperature dependence of $k_{g,\ MBr}$ was adopted as[9]

$$k_{g,MBr}(T) = k_{g,MBr}(T_r)\exp\left(\frac{T-T_r}{RTT_r}E_a\right) \qquad (8)$$

where T_r (K) is the reference temperature, R is the universal gas constant ($=8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$), T is ambient temperature (K), and E_a is the activation energy ($=2.3634\times10^4\ \mathrm{J\ mol^{-1}}$). The diffusion coefficient of MeBr in the soil for a given temperature was determined considering soil tortuosity effects and including temperature dependence of the diffusion coefficient in free air (= 325 cm^2 h^{-1} at 20 °C)[14] as[9]

$$D^{g}_{\mathrm{MBr}}(T) = \tau_{\mathrm{a}} 3600 * 4.99432E - 06T^{1.75} \tag{9a}$$

$$\tau_{\mathrm{a}} = \frac{\theta_{\mathrm{a}}^{7/3}}{\theta_{\mathrm{s}}^{2}} \tag{9b}$$

where T_a is soil tortuosity and θ_S (cm^3 cm^{-3}) is the porosity. Temperature-dependence of diffusion coefficients for MeBr in the soil solution was defined from data reported by Maharajh and Walkley.[25] As information is currently unavailable for temperature dependence of the hydrolysis rate coefficient ($\mu_{L,\ MBr}$), a fixed value of 0.014 h^{-1} was used.[14]

Literature searches to obtain a complete data set for composite testing of all the features in the model as a single unit were unsuccessful. However, successful testing of individual model components with observed data and analytical solutions provided confidence in the application of model simulations presented in this work.[21,22] The numerical solution of coupled heat and water transport was tested with experimental data of Nassar and Horton.[26] Nassar and Horton conducted laboratory experiments of heat and mass transfer with controlled temperature gradients in sealed columns (14 cm in length) of silt loam with initially uniform water content (0.12). The column ends were subjected to different temperatures (19.0 °C and 9.4 °C) in order to create a temperature gradient. The experiment was run for a period of 31 days. The numerical solution agreed well with the observed data everywhere except in the vicinity of the cold end. Since the computed mass balance error was less than 1.0%, the possibility exists of a small error in the measurement of either initial or final water contents during the experiment.

The mathematical accuracy of 2-D numerical simulation for isothermal solute transport during steady state unidirectional ground water flow in a homogenous, isotropic porous medium was tested with an analytical solution given by Leij and Bradford.[27] The capacity of the numerical solution in simulating gas transport was tested against an analytical solution given by Crank[28] considering constant water content in a homogenous 1-D soil column, for a gaseous chemical species undergoing hydrolysis. The numerical solutions duplicated the analytical solutions almost exactly in all the cases.[21,22]

3 METHODOLOGY

Arredondo fine sand (loamy, siliceous, hyperthermic Grossarenic Paleudults), a coarse-textured soil located at the IFAS (Institute of Food and Agricultural Sciences, University of Florida) Green Acres farm near Gainesville, FL, commonly found throughout north central Florida, was selected for the modeling investigation. Representative soil properties (Table 2) were taken from Carlisle *et al.*[29] The soil profile consisted of five horizons: Ap (0–23 cm); E1 (23–66 cm); E2 (66–99 cm); Bt1 (99–165 cm); and Bt2 (165–203 cm). Weather data for model simulations were taken from a weather station located at the Green Acres Farm of IFAS 15 km west of the main campus in Gainesville. February was selected for all simulations, since MeBr fumigations are typically performed in the Gainesville area around that time of the year.

A spatial profile discretization of the cross-sectional area of a single soil bed with an associated furrow resulted in 2782 elements with 1474 nodes (Fig 1). The bed was assumed to be covered with a black, low-density polyethylene (LDPE) film commonly used for mulching in Florida. Bed symmetry was assumed, so that only a half-section (ab-bc-cd-de-fe-af) of the bed and adjacent soil was required for simulations. No-flow boundary conditions were defined for heat, water, and solutes on the left- and right-hand sides of the system (af and de). The de and af boundaries represent vertical symmetry lines. The lower boundary (fe) was designated as a zero thermal-gradient boundary condition, with gravitational water flow (ie unit gradient of total hydraulic head).

For chemical transport, both convective (in the liquid phase) and diffusive (both in the aqueous liquid and gaseous phases) transports were allowed across the bottom boundary (fe), with the assumption that solute leaving the lower boundary is lost from the flow domain to underlying soil and groundwater (ie there is no return flow). Emission loss of MeBr from the soil to the atmosphere across the top boundary (ab-bc) was described through diffusive flux, assuming a 1-cm thick boundary layer and zero concentration on the

Table 2. Physical properties and parameter values for a profile of Arredondo fine sand soil

Soil layer	*Sand (%)*	*Silt (%)*	*Clay (%)*	*OC*[a] *(%)*	K_{a1}[b] *(cm^{-3} g^{-1})*	*BD*[c] *(g cm^{-3})*	K_{sat}[d] *(cm h^{-1})*
Ap	91.9	3.3	4.8	0.83	0.1826	1.52	6.2
E1	92.0	3.3	4.7	0.28	0.0616	1.54	16.7
E2	91.4	3.0	5.6	0.14	0.0308	1.52	15.1
Bt1	86.0	3.7	10.3	0.11	0.0242	1.56	6.4
Bt2	75.2	3.0	21.8	0.20	0.0440	1.57	2.4

[a] Organic carbon.
[b] Soil sorption coefficient for MeBr estimated from K_{oc} value presented in Table 1.
[c] Bulk density.
[d] Saturated soil hydraulic conductivity.

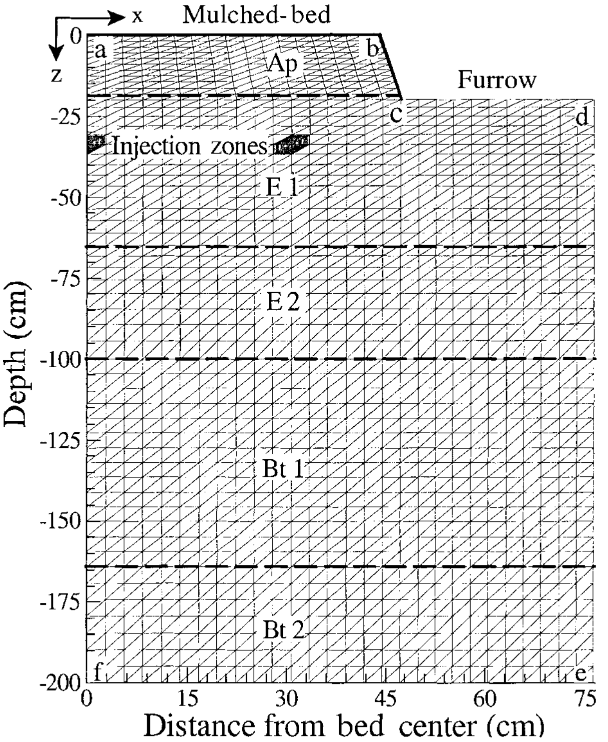

Figure 1. Schematic of the simulation domain showing soil layers and methyl bromide injection points.

atmospheric side of the boundary layer. These emission fluxes may be defined explicitly as

$$\mathcal{J}_{\text{gas}}^{\text{Bed}} = -\left[D_{\text{plastic}}^{\text{g}}\left(\frac{g_s - g_{s+1(\text{air})}}{z_s - z_{s+1(\text{air})}}\right)\right] \tag{10}$$

for the plastic-mulched soil bed, and

$$\mathcal{J}_{\text{gas}}^{\text{Furrow}} = -\frac{1}{2}\left[D_{\text{freeair}}^{\text{g}}\left(\frac{g_s - g_{s+1(\text{air})}}{z_s - z_{s+1(\text{air})}}\right) + \theta_{\text{a}} D_{\text{soil}}^{\text{g}}\left(\frac{g_{s-1} - g_s}{z_{s-1} - z_s}\right)\right] \tag{11}$$

for the un-mulched soil furrow. Here $\mathcal{J}(\text{g cm}^{-2}\,\text{h}^{-1})$ is the emission flux, $D(\text{cm}^2\,\text{h}^{-1})$ is the diffusion coefficient, $g(\text{g cm}^{-3})$ is the gaseous MeBr concentration, z (cm) is the vertical location, and the subscripts $_{s,\ s+1}$, and $_{s-1}$ represent nodes at the soil surface, above the surface, and below the surface, respectively. The diffusion coefficient for MeBr transport through the plastic mulch was defined by eqn (8) using $E_{\text{a}} = -3.3166 \times 10^4$ (J mol^{-1}) and $D_{\text{plastic}}^{\text{g}}$ at $T_{\text{r}} = 22.5$ (°C) being 191.641 (cm^2 h^{-1}) as described by Wang *et al.* [9]

Average weather parameters used in simulations for the month of February were: (1) average daily temperature = 11.6 °C, (2) temperature amplitude = 7.7 °C, (3) wind velocity = 11.0×10^4 cm h^{-1}, (4) day-length = 11.0 h, and (5) global daily radiation = 1400 J cm^{-2} day^{-1}.

The MeBr fumigant was assumed to be applied at a rate of 450 kg ha^{-1} (standard practice) using a three-shank applicator, such that one and a half shanks of injection occurred within the flow domain shown in Fig 1. Injection depths for the simulations were set at 33 cm (shallow; a standard practice), 50 cm and 66 cm, and time of MeBr application was set at 0900 h. An initially water-saturated soil profile (without mulch cover) was allowed to drain and evaporate during simulation. Four water saturation profiles (percentage by volume) were then selected for investigation to provide different soil water regimes: (1) WS1–54%, (2) WS2–46%, (3) WS3–38% and (4) WS4–30%. Mass- and energy-balance errors were less than 2.0% for all simulations reported in this work.

4 MODEL SIMULATIONS

4.1 Non-isothermal versus isothermal soil conditions

Isothermal simulations were performed in order to compare with non-isothermal simulations existing under a black LDPE mulch. The isothermal chemical transport (involving the D^{g}, D^{L}, k_{g}, $D_{\text{plastic}}^{\text{g}}$ parameters) was kept independent of temperature fluctuations. The parameters for chemical transport were estimated and kept constant for a daily average temperature of 11.6 °C, typically existing during the month of February in the vicinity of Gainesville, FL (diffusion coefficient in air = 308 cm^2 h^{-1}, Henry's Law constant = 0.15). Isothermal simulations were also performed with parameters not adjusted to average daily field temperature, as is the usual practice in conducting isothermal simulations, at 22.5 °C.

The isothermal and non-isothermal simulations conducted for the first 7 days after injection showed (Fig 2) that MeBr emission fluxes from both bed and furrow were affected by non-isothermal conditions. Figure 2 (mulched top) shows that, in the case of non-isothermal simulations for black LDPE, diurnal fluctuations in MeBr emissions from bed and furrow followed a diurnal temperature pattern, whereas a similar cyclical nature for MeBr emissions was missing in isothermal simulations. This emission pattern has been reported earlier for field investigations.[5,18] Higher diffusive flux rates for MeBr were predicted initially from the furrow, which subsequently flattened out due to lower concentration gradients as increasing amounts of MeBr were lost to the atmosphere. The delay in reaching the initial peak emission flux (Fig 2) from the bed occurred due to a build-up time for MeBr concentrations beneath the mulch and an increase in temperature of the plastic mulch as the day progressed (application time, 09000 h), whereas the bare furrow surface offered a rapid interchange with atmosphere.

The results suggest that inclusion of non-isothermal conditions is essential to estimate correctly the fate and transport of volatile chemicals. Exclusion of temperature effects on solute transport may predict (Table 3) material losses to the atmosphere incorrectly in the case of chemicals such as MeBr. Though isothermal simulations conducted with transport parameters estimated and held constant at average field temperature (11.6 °C) did not show differences in total

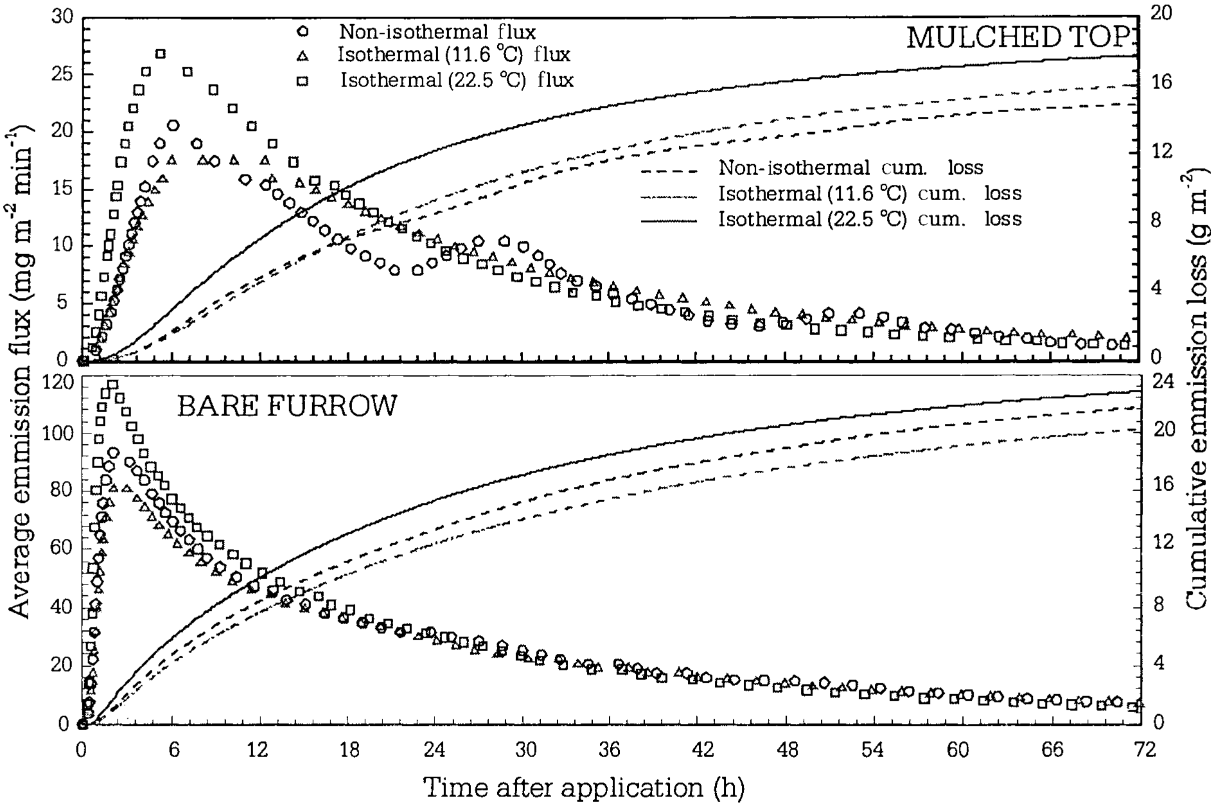

Figure 2. Simulated emission fluxes of methyl bromide through the bed under isothermal and non-isothermal transport of fumigant.

Table 3. Material balances (%) of methyl bromide under different fumigation scenarios

Soil water Saturation (% v/v)	Day 1				Day 3				Day 7			
		Emission				Emission				Emission		
	Soil	Furrow	Bed	Hydrolyzed	Soil	Furrow	Bed	Hydrolyzed	Soil	Furrow	Bed	Hydrolyzed
Injection at 33 cm depth, non-isothermal simulation												
54	71	10	7	12	32	21	20	27	8	28	26	39
46	66	14	10	11	28	26	23	23	7	32	28	33
38	59	20	13	8	23	33	25	18	5	39	29	26
30	55	24	15	7	21	38	26	15	5	44	29	22
Injection at 50 cm depth, non-isothermal simulation												
54	77	6	2	15	38	18	11	33	10	25	17	48
46	74	10	4	13	35	23	14	29	9	30	19	42
38	68	15	6	10	29	31	17	24	7	38	21	34
30	64	19	8	9	26	36	18	20	7	43	22	29
Injection at 65 cm depth, non-isothermal simulation												
54	81	3	0	17	44	12	6	38	12	20	11	56
46	79	5	1	15	40	18	9	34	11	26	14	49
38	75	10	3	12	34	25	12	28	9	34	16	41
30	72	14	4	10	32	31	13	24	8	39	18	35
Injection at 33 cm depth, isothermal (22.5 °C) simulation												
54	62	13	13	11	25	25	27	23	6	30	31	32
46	57	17	16	9	22	29	29	20	5	34	33	27
38	49	23	20	7	18	36	31	15	4	41	34	21
30	46	27	21	6	16	40	31	13	4	45	34	18
Injection at 33 cm depth, isothermal (11.6 °C) simulation												
54	70	10	8	13	32	20	21	27	8	26	27	39
46	66	13	11	11	28	24	24	23	7	30	29	33
38	59	18	15	8	23	31	27	18	5	37	31	26
30	55	22	16	7	21	36	28	15	5	41	32	22

(including the bed and furrow) material loss to the atmosphere compared with non-isothermal simulations (Table 3), the magnitude of MeBr loss from either bed or furrow for the isothermal and non-isothermal simulations did not match when compared separately. This implies that over-estimation (in the case of a mulched surface) and under-estimation (in the case of a bare surface) may result if non-isothermal conditions are ignored. However, when the transport parameters were not adjusted to average field temperature and held constant at 22.5 °C (presumed normal laboratory temperature where constants are usually determined), isothermal simulations showed over-estimation of material MeBr loss through both mulched and bare surfaces (Fig 2 and Table 3).

4.2 Variable water saturation of soil

Volumetric water contents present in the soil bed at the time of fumigation not only affect the hydrolysis of MeBr but also affect its transport in the soil. Four different water saturation regimes were investigated during the simulations. The simulations revealed (Fig 3, shown for an injection depth of 33 cm) that larger amounts of MeBr were lost to the atmosphere when there was less water (WS4–30% <WS3–38% <WS2–46% <WS1–54%) in the soil profile. This result was expected, due to less hydrolysis and enhanced diffusion. This resulted in a higher MeBr emission flux from both the bed and furrow in the case of the drier (WS3–38% and WS4–30%) profile. The emission fluxes from the bed were higher (Fig 3) during the later periods (after ≈34 h) in WS1–54%. This was due to the higher water contents in WS1–54%, causing larger amounts of MeBr to partition into the aqueous phase, which were then released to the gaseous phase as atmospheric losses occurred in order to maintain equilibrium between the aqueous and gaseous phases (controlled by the Henry's Law constant).

Temperatures under the bed and at the bare soil surface (not shown) were higher in WS3–38% and WS4–30% as compared to WS1–54% and WS2–46%, whereas water contents were lower at the same locations. The wetter profiles maintained a higher water content at the mulched soil surface, due to vapor movement and condensation. This also contributed to smaller emissions of MeBr through both bed and furrow surfaces due to a partial blockage of soil pores with water. Though not shown, simulations reveal that a cyclical diurnal pattern in the temperature existed in the soil profile. This demonstrates that MeBr fate and transport would be affected by non-isothermal conditions within the bed.

Material balances after fumigant injection indicated that more MeBr was hydrolyzed in the wetter profile (WS1–54%), as would be expected. During the first day following injection, a 15–22% higher emission loss to the atmosphere (Table 3) was predicted in the drier soil system (WS4–30%) compared with the wet profile (WS1–54%) at the different fumigant injection depths. By the end of the third day, the amount of MeBr retained in the wet profile (WS1–54%) was 10–12% more than that in the drier one (WS4–30%). However,

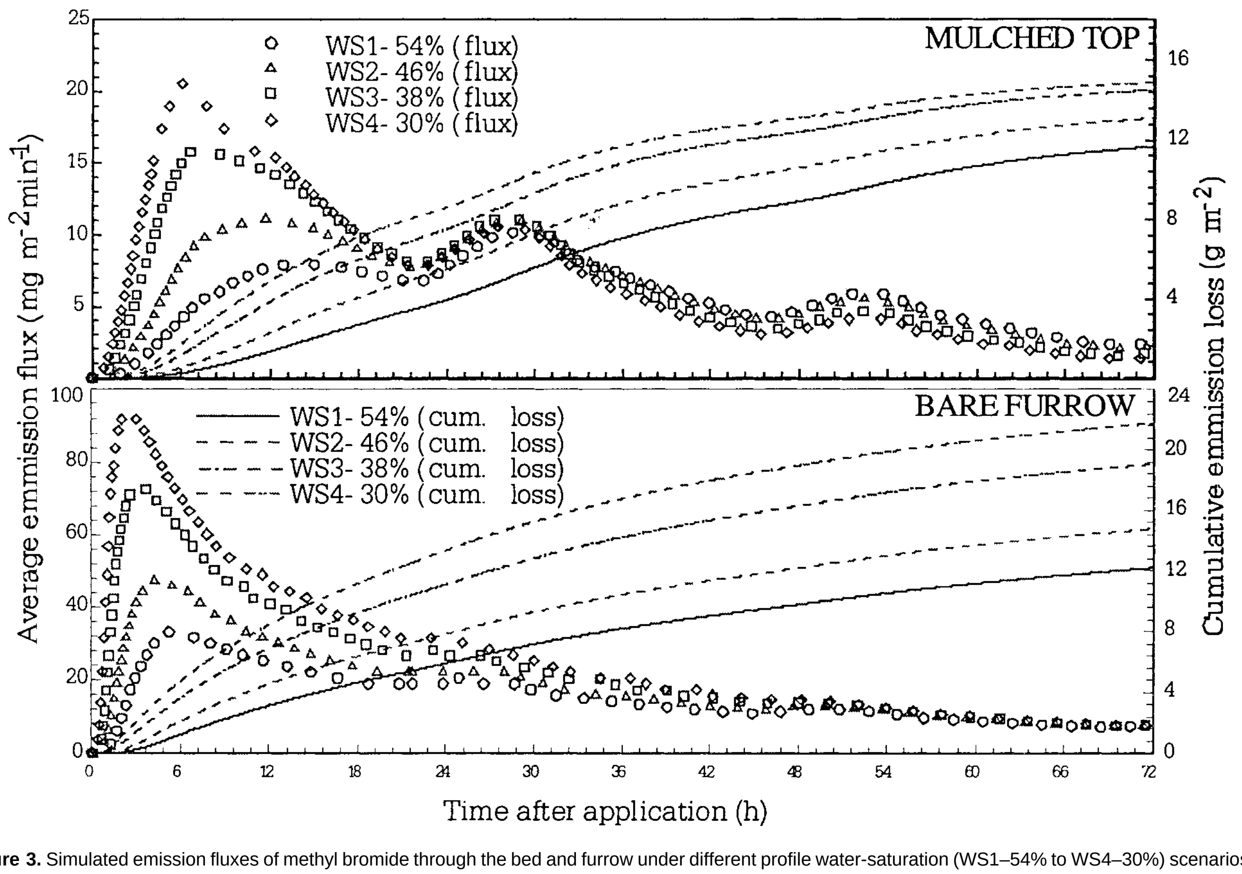

Figure 3. Simulated emission fluxes of methyl bromide through the bed and furrow under different profile water-saturation (WS1–54% to WS4–30%) scenarios.

12–14% more MeBr was hydrolyzed in the wet profile (WS1–54%) than that in the drier one (WS4–30%) over a 3-day period (Table 3). This indicates that the wet profile was able to retain more MeBr than the dry one, but resulted in more bromide formation as a decomposition product. The higher retention of MeBr in a saturated soil profile was partly due to smaller quantities of available diffusion volume in the gaseous phase, and partly due to more MeBr partitioning into the aqueous phase at the higher water contents. Diffusion of MeBr in the aqueous phase was very slow compared to the gaseous phase (by a factor of 10^3).

4.3 Depth of fumigant injection

Influence of depth of the fumigant injection zone upon MeBr distribution and loss was investigated using three injection depths, 33 cm (shallow), 50 cm and 66 cm (deep). Results for the shallow (33 cm) injection depths with variable water saturation are presented in Fig 3. In the case of deeper injection of MeBr at 50 and 66 cm (Fig 4, shown for WS4–30%), emission fluxes were smaller than those for the 33-cm injection zone. This was partly due to higher water contents in the deeper injection zone arising from the presence of a differential soil horizon (Fig 1), resulting in more MeBr in the aqueous phase, and also to greater distance to the emission surface from the center of MeBr mass.

Negligible amounts of MeBr were lost to the atmosphere during the first day in the wettest profile (WS1–54%) with deeper injection (66 cm), and only 23% less was lost compared with shallow (33 cm) injection by 3 days following injection. Also, in the case of the driest soil system (WS4–30%), deepest injection resulted in less than 20% emission (Table 3) to the atmosphere compared to the shallower injection depth of 33 cm over the first 3 days after injection. Thus, deeper injection is potentially conducive to controlling atmospheric emissions of MeBr, irrespective of profile wetness.

4.4 Efficiency of fumigation

Soil sterilization during fumigation was investigated based on the toxic level of MeBr (20 mg litre^{-1} or greater) and exposure time (minimum 24 h) for second-stage juveniles of root knot nematode.[30] Effective soil fumigation is achieved when the target pathogen and/or pest are successfully eradicated from the desired soil zones to provide economically viable yields. Optimum fumigant dosage and method of application must be determined when a fumigant such as MeBr is environmentally hazardous. Data from Mckenry and Hesse[30] were used as a basis for investigating soil sterilization efficiency for different scenarios. To identify the eradication zones for root knot nematode, contour plots in the soil bed were used to demarcate those zones which satisfied the conditions of exposure time (24 h) for the related level of exposure concentration ($\geq$20 mg litre^{-1}). Figure 5 shows the demarcated contoured zones fulfilling the criterion based on Mckenry and Hesse.[30] The current practice of mulching the bed with shallow (33 cm) injection provides reasonably adequate sterilization (Fig 5, contour numbers 1 to 4, representing WS1–

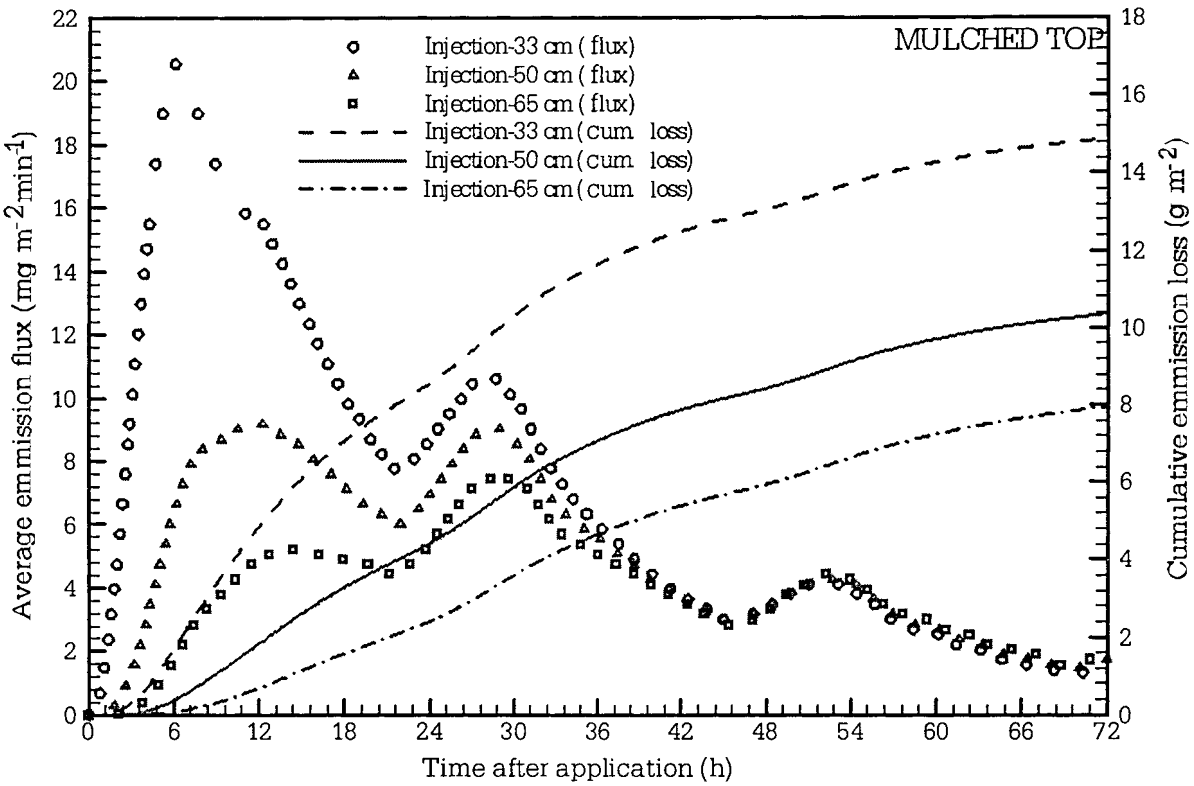

Figure 4. Simulated emission fluxes of methyl bromide through the bed under different depths of fumigant injection.

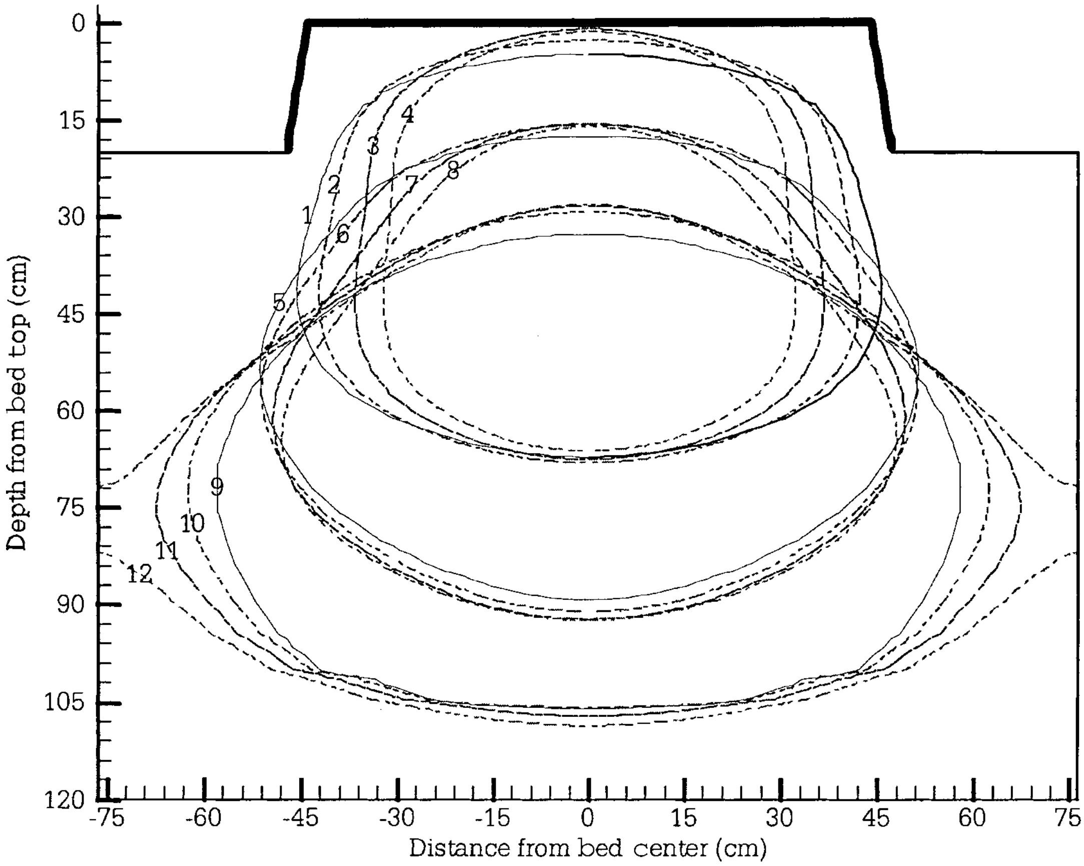

Figure 5. Simulated soil sterilization contours under different depths of fumigant injection and for varying levels of soil wetness: (a) injection depth=33 cm, contour numbers 1 to 4 representing WS1–54% to WS4–30%, respectively, (b) injection depth=50 cm, contour numbers 5 to 8 representing WS1–54% to WS4–30%, respectively and (c) injection depth=65 cm, contour numbers 9 to 12 representing WS1–54% to WS4–30%, respectively.

54% to WS4–30%, respectively) seemingly irrespective of soil profile wetness if a single crop row were grown in the center of the bed. It was very clear, from this analysis, that deep injection (50 and 65 cm) in either dry or wet soil does not provide adequate soil sterilization in the root zone where it is desired (Fig 5, contour numbers 5 to 8, representing WS1–54% to WS4–30%; respectively for injection depth of 50 cm and contour numbers 9 to 12, representing WS1–54% to WS4–30%, respectively for injection depth of 66 cm).

5 CONCLUSIONS

A numerical investigation conducted using a coupled heat-water flow and chemical transport model to analyze the fate and transport of MeBr during fumigation of soil beneath plastic-mulched beds provided improved insight into the dynamics of MeBr fumigation in relation to critical management and environmental impacts. Non-isothermal soil conditions were shown to be especially important for chemical transport in plastic-mulched soil beds, particularly where highly volatile chemicals like MeBr are used for soil fumigation. Chemical transport parameters adjusted to field-average temperature (11.6 °C) under isothermal simulations showed material loss (bed + furrow) similar to that for non-isothermal simulations. However, unadjusted transport parameters (kept constant at 22.5 °C) resulted in over-estimation of MeBr loss from both the mulched bed and the bare furrow. Considering non-isothermal conditions is thus important in the case of highly volatile chemicals that involve gaseous transport. Wetter soil profiles at all injection depths helped retain MeBr in the soil with fewer emission losses to the atmosphere, but also resulted in more bromide production as a decomposition product, due to increased hydrolysis. Increasing the injection depth reduced atmospheric MeBr emissions; however, efficiency of sterilizing the crop root zone using the criteria for root knot nematode juveniles was drastically reduced.

The simulation modeling of MeBr fumigation in bedded, mulched vegetable/fruit production systems revealed that current practice provides adequate sterilization of the crop root zone before planting. However, increasing moisture content of the soil could help to reduce emission and retain MeBr for a longer period within the soil. Different results can be expected for varied weather conditions, moisture status of the soil at the time of fumigation, depth of injection, and mulched bed to uncovered furrow area ratio of the fumigated field. The results (emission fluxes and overall emission) of this numerical investigation are of similar orders of magnitude to those reported in field observations given the conditions (weather, and soil moisture status) for which simulations were carried out.[5–10] However, carefully controlled field experiments are needed to validate and confirm conclusions based upon the model simulations.

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